

Our Ref.: 925-222  
534570

# ***U.S. PATENT APPLICATION***

***Inventor(s):*** Toshiyuki Tohda

***Invention:*** SEMICONDUCTOR DEVICE AND PROCESS FOR MANUFACTURING THE  
SAME

***NIXON & VANDERHYE P.C.  
ATTORNEYS AT LAW  
1100 NORTH GLEBE ROAD  
8<sup>TH</sup> FLOOR  
ARLINGTON, VIRGINIA 22201-4714  
(703) 816-4000  
Facsimile (703) 816-4100***

## ***SPECIFICATION***

## SEMICONDUCTOR DEVICE AND PROCESS FOR MANUFACTURING THE SAME

## BACKGROUND OF THE INVENTION

Field of the Invention

5           The present invention provides a capacitor for a  
ferroelectric memory and the like, and a process for  
manufacturing the same. More particularly, the present  
invention relates to a process for manufacturing a semiconductor  
device which has a capacitor comprising a lower electrode layer,  
10 a ferroelectric layer and an upper electric layer, which can  
suppress a peeling between the layers while maintaining  
electrical properties of the ferroelectric layer.

Prior Art

15           Recently, a ferroelectric memory has focused attention  
in a semiconductor field. A ferroelectric memory is a memory  
in the next generation which is characterized by a quick  
response, a random access, multiple rewriting, a low  
consumption power and the like. In the current ferroelectric  
20 memory, a transistor is formed, followed by formation of a  
capacitor comprising an electrode and a ferroelectric layer.  
These steps are usual processes as described in the Example of  
JP-A 11-214655. An embodiment of the prior art will be  
explained using Figures 5 and 6 below.

25           First, on an underlying substrate 21 on which a transistor

has been formed, an adhesion layer **22** is deposited to 50 nm by sputtering, for example,  $\text{TiO}_2$ ,  $\text{TiN}$  and the like. A lower electrode layer **23** is deposited thereon to 200 nm by sputtering, for example,  $\text{Pt}$ ,  $\text{Ir}$ ,  $\text{IrO}_3$  and the like. In addition, for example, SBT, PZT and the like is deposited by a Sol-Gel method, MOD, LSMC, sputtering, CVD and the like to 200 nm to form a ferroelectric layer **24** thereon, and which is sintered in an  $\text{O}_2$  atmosphere. Further, an upper electrode layer **25** is deposited thereon to 100 nm by sputtering, for example,  $\text{Pt}$ ,  $\text{Ir}$ ,  $\text{IrO}_3$  and the like (Figure 5A).

After that, a 1.5- $\mu\text{m}$  thick photoresist pattern **26** for processing the upper electrode is formed on the upper electrode layer **25** and, then, the upper electrode **25** is processed by dry etching (Figure 5B). Dry etching is performed mainly by sputter etching with Ar by highly dissociating a mixture gas of  $\text{Cl}_2$  and Ar under a high vacuum at 3 mTorr or less, for example, on a high density plasma etching apparatus using an Inductive Coupling Plasma (ICP) and the like. Generally, since vapor pressures of Pt and Ir are very low due to their low reactivity, Pt and Ir dissociated by sputter etching re-adhere to a sidewall of the pattern even after etching. By adding  $\text{Cl}_2$ ,  $\text{F}_2$  and the like to the etching gas, materials adhering on the sidewall are converted to chlorine or fluorine and the like so that they can be removed in the later step of washing.

Then, an etching depot **27** adhering to the sidewall of the

pattern is removed and, subsequently, a remaining resist pattern is removed by using a down flow  $O_2$  ashing apparatus and the like (Figure 5C).

Subsequently, a 2.0- $\mu m$  thick photoresist pattern 28 for processing a ferroelectric layer is formed on the processed upper electrode layer 25 and the ferroelectric layer 24, and the ferroelectric layer 24 is processed by dry etching (Figure 5D). Since a ferroelectric layer has similar etching properties to those of Pt, Ir and the like, etching is performed under similar conditions and by a similar mechanism to those for etching the upper electrode layer.

After that, the etching depot 29 adhering to the pattern side wall is removed by washing and, then, a remaining resist is removed by down flow  $O_2$  ashing and the like (Figure 6E).

Similarly, a 2.0- $\mu m$  thick photoresist pattern 30 for processing a ferroelectric layer is formed on the processed upper electrode layer 25, the processed ferroelectric layer 24 and the lower electrode layer 23, and the lower electrode layer 23 is processed by dry etching (Figure 6F).

Since the lower electrode layer is made from a similar material to that for the upper electrode layer, etching is performed by using a similar condition and mechanism.

After that, the etching depot 31 adhering to the pattern side wall is removed by washing and, then, a remaining resist is removed by down flow  $O_2$  ashing and the like (Figure

6G) .

When the capacitor shape is formed according to the above steps, the ferroelectric properties are deteriorated by dry etching and washing. Therefore, at the last step, after processing the capacitor, the ferroelectric layer is re-sintered by annealing at a temperature as high as or higher than the firing (or sintering) temperature at which the ferroelectric layer is formed, to recover its electrical properties. By undergoing the above steps, the capacitor of the ferroelectric layer is formed.

However, this conventional process has a problem that a layer-peeling phenomenon occurs between an electrode layer and a ferroelectric layer when a capacitor is formed.

The layer-peeling phenomenon occurs when a depot is washed after etching each of the layers, and in a final annealing. Therefore, it can be considered that a lift-off phenomenon caused by penetration of a solution for washing a depot into a gap between the electrode layer and the ferroelectric layer, and interlayer separation due to a difference in a layer shrinkage rate between the electrode layer and the ferroelectric layer in annealing directly result in the layer peeling.

From an examination of the conventional semiconductor devices, it is demonstrated that peeling of the upper electrode layer tends not to occur as the surface morphology of the ferroelectric layer is worse, and that as the better surface

morphology of the ferroelectric layer, that is, the denser film density results in the better electric properties. Therefore, it is currently difficult to accomplish to improve electrical properties and to decrease film peeling simultaneously, resulting in a big problem.

#### SUMMARY OF THE INVENTION

Against the above problem, although a method is proposed for preventing the peeling by putting a dielectric layer with a high adherability between the electrode layer and the ferroelectric layer, it has disadvantages such as deterioration in electrical properties of the ferroelectric layer, process complication and the like and, therefore, an optimal method has not been established yet.

Thus, an object of the present invention is to suppress the peeling phenomenon in a semiconductor device comprising at least a ferroelectric layer and an upper electrode formed thereon while maintaining the electrical properties of the ferroelectric layer.

According to the present invention, since a convex or concave region is formed on a surface of a first layer by etching, peeling between the first layer on which the convex or concave region has been formed and an upper layer formed on the first layer, which is caused by penetration of a bath or a layer shrinkage in a step of heating, is prevented (referred to as

an "anchor effect").

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a cross-sectional view illustrating a semiconductor device of an embodiment according to the present invention.

Figure 2 is a cross-sectional view illustrating a step of manufacturing a semiconductor device of an embodiment according to the present invention.

Figure 3 is a cross-sectional view illustrating a step of manufacturing a semiconductor device of an embodiment according to the present invention.

Figure 4 is a cross-sectional view illustrating a step of manufacturing a semiconductor device of an embodiment according to the present invention.

Figure 5 is a cross-sectional view illustrating a step of manufacturing a semiconductor device according to a conventional technique.

Figure 6 is a cross-sectional view illustrating a step of manufacturing a semiconductor device according to a conventional technique.

Figure 7 is a schematic illustration showing film peeling which occurs in a conventional semiconductor device.

#### DETAILED DESCRIPTION OF THE INVENTION

Detailed process will be explained below.

First, a problem of peeling between an upper electrode and a ferroelectric layer beneath the upper electrode layer is explained. After a ferroelectric layer is formed, a resist pattern is formed on a region in which the upper electrode is processed and formed. The ferroelectric layer is, then, etched to make a convex pattern on the surface of the ferroelectric layer. The size of this pattern should be controlled so that the convex pattern does not lap over outside of the upper electrode pattern in the subsequent step of forming the upper electrode with considering fluctuation in a pattern line width, an alignment deviation and the like. That is, a line width of the resist pattern for making the convex pattern is made to be narrower than the minimal line width of the upper electrode by a margin for the alignment deviation.

An etching depth of the ferroelectric layer is adjusted to the thickness of the upper electrode or smaller, since when the etching depth is larger than the thickness of the upper electrode, the upper electrode cannot be sputtered successfully, and the etching depth of the ferroelectric layer is adjusted to half of the thickness of the upper electrode or larger in order to exhibit the anchor effect. Further, from the viewpoint of the electrical properties of the ferroelectric layer, it is required that the etching depth of the ferroelectric layer is adjusted to half of its thickness or smaller.



After etching the ferroelectric layer, a depot and the remaining resist layer are removed by washing and ashing and, then, an upper electrode is formed by sputtering. By carrying out subsequent processes after the formation of the upper electrode, peeling can be prevented due to the anchor effect as compared with the case where the upper electrode attaches a smooth ferroelectric layer. The above-mentioned means can be applied to an interface between the lower electrode and the ferroelectric layer to obtain the anchor effect.

#### Example

The present invention will be explained in detail based on the following Examples.

A semiconductor device according to the Example of the present invention is shown in Figure 1. As shown in Figure 1, the semiconductor device of the present invention is characterized in that an upper electrode 17 and a ferroelectric layer 14 have a convex region. By this constitution, a layer peeling can be suppressed. In this Example, one convex region is formed on one layer, but a plurality of convex regions may be formed on one layer. Alternatively, a concave region may be formed in place of the convex region.

Figures 2A ~ D, Figures 3E ~ H, and Figures 4I ~ K are schematic illustrations showing procedures for manufacturing the semiconductor device shown in Figure 1.

First, on a semiconductor substrate 11 on which a transistor is formed and which is covered with an insulation layer, an adhesion layer 12 is deposited to 50 nm, for example, by sputtering  $\text{TiO}_2$ ,  $\text{TiN}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TaSiN}$  and the like. These layers may also be obtained by forming a Ti, Al, TaSi layer and the like by sputtering, and oxidizing or nitridizing.

A lower electrode layer 13 is deposited thereon to 200 nm, for example, by sputtering Pt, Ir,  $\text{IrO}_3$  and the like. A ferroelectric layer 14 having a thickness of 200 nm is formed by repeating a step of coating, for example,  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  (SBT) by a metal organic deposition (MOD) method and a step of calcining it under an oxygen atmosphere for 30 minutes or longer at 650 °C or higher (Figure 2A). A method of forming a ferroelectric layer other than MOD includes a sol-gel process, a liquid source misted chemical vapor deposition (LSMCVD), sputtering, a chemical vapor deposition process (CVD) and the like.

After that, a photoresist is applied on the ferroelectric layer 14 at a thickness of 2  $\mu\text{m}$  by spin-coating. Then, a photorecticle for fabricating the upper electrode is used and its alignment is adjusted to a region where an upper electrode is formed in a subsequent step. A resist pattern 15 is formed in the steps of exposing and developing (Figure 2B). The pattern size is smaller than the minimum value of the upper electrode size by a margin for an alignment shift. That is, if a specification for the upper electrode size is within 1.0  $\mu\text{m} \pm$

0.1  $\mu\text{m}$  and that for the alignment shift is 0.2  $\mu\text{m}$ , the specification for the resist pattern size is then within 0.7  $\mu\text{m}$ .

Subsequently, the resist pattern 15 is used as a mask to etch the ferroelectric layer 14 (Figure 2C). As etching conditions, for example, a high density plasma ICP etcher is used and the settings are as follows: Source power 2000 W; Bias power 500 W; Pressure 3 mTorr;  $\text{Cl}_2/\text{Ar}$  flow rate 30/90 sccm; and Etching depth 50 nm or greater and below 100 nm.

After etching, an etching depot 16 adhering to the pattern sidewall is removed by washing (e.g., by dipping into 10% concentration hydrochloric acid for 30 seconds) and, then, the remaining resist pattern 15 is removed by ashing (e.g., on a microwave down flow ashing apparatus: Microwave power 1000 W; Wafer temperature 250  $^{\circ}\text{C}$ ;  $\text{O}_2$  flow rate 1000 sccm; Treatment time 3 minutes) (Figure 2D).

An upper electrode layer 17 is formed on the ferroelectric layer 14 thus fabricated by depositing, for example, Pt, Ir,  $\text{IrO}_3$ , and the like at a thickness of 100 nm by a conventional method such as sputtering (Figure 3E).

Next, a photoresist is applied on the upper electrode 17 at a thickness of 1.5  $\mu\text{m}$  by spin-coating. Then, a photoreticle for fabricating the upper electrode is used to expose and develop the photoresist in order to form a resist pattern 18. Subsequently, the resist pattern 18 is used as a mask to etch the upper electrode layer 17 (Figure 3F). As etching conditions,

for example, a high density plasma ICP etcher is used and the settings are as follows: Source power 2000 W; Bias power 500 W; Pressure 3 mTorr; Cl<sub>2</sub>/Ar flow rate 30/90 sccm; and Etching depth 115 nm (15% overetching based on the thickness of the upper electrode with considering a thickness fluctuation 10% and a etching rate fluctuation 10%).

After etching, an etching depot **19** adhering to the pattern sidewall is removed by washing (e.g., by dipping into 10% concentration hydrochloric acid for 30 seconds) and, then, the remaining resist pattern **18** is removed by ashing (e.g., on a microwave down flow ashing apparatus: Microwave power 1000 W; Wafer temperature 250 °C; O<sub>2</sub> flow rate 1000 sccm; Treatment time 3 minutes) (Figure 3G).

Next, a photoresist is applied at a thickness of 1.5 μm by spin-coating. Then, a reticle for fabricating the ferroelectric layer is used to expose and develop the photoresist in order to form a resist pattern **1a**. Subsequently, the resist pattern **1a** is used as a mask to etch the ferroelectric layer **14** (Figure 3H). As etching conditions, for example, a high density plasma ICP etcher is used and the settings are as follows: Source power 2000 W; Bias power 500 W; Pressure 3 mTorr; Cl<sub>2</sub>/Ar flow rate 30/90 sccm; and Etching depth 115 % based on the thickness of the remaining ferroelectric layer.

After etching, an etching depot **1b** adhering to the pattern sidewall is removed by washing (e.g., by dipping into 10%

concentration hydrochloric acid 30 seconds) and, then, the remaining resist pattern 1a is removed by ashing (e.g., on a microwave down flow ashing apparatus: Microwave power 1000 W; Wafer temperature 250 °C; O<sub>2</sub> flow rate 1000 sccm; Treatment time 3 minutes) (Figure 4I).

Next, a photoresist is applied thereon at a thickness of 2.0 μm by spin-coating. Then, a photorecticle for fabricating the lower electrode is used to expose and develop the photoresist in order to form a resist pattern 1c. Subsequently, the resist pattern 1c is used as a mask to etch the lower electrode layer 13 (Figure 4J). As etching conditions, for example, a high density plasma ICP etcher is used and the settings are as follows: Source power 2000 W; Bias power 500 W; Pressure 3 mTorr; Cl<sub>2</sub>/Ar flow rate 30/90 sccm; and Etching depth 230 nm (15% overetching based on the thickness of the upper electrode with considering a thickness fluctuation 10% and a etching rate fluctuation 10%).

After etching, an etching depot 1d adhering to the pattern sidewall is removed by washing (e.g., by dipping into 10% concentration hydrochloric acid 30 seconds) and, then, the remaining resist pattern 1c is removed by ashing (e.g., on a microwave down flow ashing apparatus: Microwave power 1000 W; Wafer temperature 250 °C; O<sub>2</sub> flow rate 1000 sccm; Treatment time 3 minutes) (Figure 4K).

Finally, in order to recover of the ferroelectric layer from a damage in the electrical properties caused by etching,

washing and ashing, annealing is performed, for example, under a N<sub>2</sub> atmosphere at 650 °C for 30 minutes.

A semiconductor device finally obtained shows high electrical performance. In addition, occurrence of peeling was not observed.

According to the present invention, a layer peeling, which occurs in a conventional process for fabricating a ferroelectric capacitor, can be effectively prevented.